

Chlorine activation near the midlatitude tropopause

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[1] We report on substantial chlorine activation near the midlatitude tropopause over the central United States (39–42°N 102–105°W) during the WB-57F Aerosol Mission (WAM) in April 1998. The extent of activation was determined by simultaneous in situ measurements of ClO and ozone and calculations of total inorganic chlorine (Cl_y) based on recently reported relationships between HCl, ozone, and halocarbons for similar latitudes. Levels of [ClO]/[Cl_y] approaching 50% occurred in a region of strong gravity wave activity, high particulate surface areas (5–20 μm² cm⁻³), low ozone, and relatively high humidities (20–25 ppm of H₂O, yet undersaturated with respect to ice), consistent with a heterogeneous mechanism on particles formed in recently lofted tropospheric air as it mixed into the lowermost stratosphere. These observations are similar to a previous one of chlorine activation on volcanic aerosol, suggesting a common heterogeneous chemical mechanism involving HCl, ClNO₃, and HOCl that even in volcanically quiescent years can impact ozone photochemistry in regions of the lowermost stratosphere influenced by mixing from the tropopause region. Models not incorporating this chlorine activation process may be underestimating the impact on ozone in the midlatitude lowermost stratosphere by decomposition of very short lived halocarbon compounds, including substitutes for ozone-depleting compounds.

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1. Introduction

[2] The midlatitude lowermost stratosphere, the tropopause region and the first few kilometers above that, exhibits characteristics not shared with the rest of the stratosphere [Holton et al., 1995]. It is a region where mixing occurs between the troposphere and stratosphere and where the relative effects of chemical and dynamical forcings on ozone trends can be comparable [World Meteorological Organization (WMO), 2003]. A substantial fraction of total column ozone mass lies in the lowermost stratosphere; trends here can have a large impact on total column ozone trends, and hence total ultraviolet (UV) radiation reaching the surface. Ozone changes near the tropopause can have a substantial impact on the radiative balance of the atmosphere as well [Lacis et al., 1990]. Negative ozone trends in the midlatitude lowermost stratosphere [Logan et al., 1999] have not yet been definitively explained by chemistry or dynamics, or some combination

of the two [WMO, 2003]. However, there are significant dynamical linkages that can impact ozone trends in the midlatitude lowermost stratosphere from both the upper tropical troposphere and the polar vortex [Tuck et al., 1992; Reid et al., 2000; Millard et al., 2002; Hadjinicolaou et al., 2005].

[3] The idea of a heterogeneous chemical influence on lowermost stratosphere midlatitude ozone trends has been proposed via analogy to the well-described ozone hole processes occurring at higher altitudes and latitudes, whereby active chlorine (or ClO_x, primarily ClO, OClO, and Cl₂O₂) is produced from more stable forms of inorganic chlorine (or Cl_y, primarily HCl, ClNO₃, and HOCl) via reactions on cirrus and background aerosol surfaces [Borrmann et al., 1996; Solomon et al., 1997]. Models have shown activation of up to 50% of reservoir chlorine, depending on latitude and season [Solomon et al., 1997; Meilinger et al., 2001], by heterogeneous reactions of HCl with ClNO₃ and HOCl on enhanced particulate surface areas. Solomon et al. [1997] showed that, if they occur frequently and in regions of relatively high total inorganic chlorine (e.g., Cl_y > 500 ppt), such levels of chlorine activation could explain the observed ozone trends at midlatitudes. Attention quickly turned to investigations of ClO abundances from archived data sets and on the possibility of particulate enhancements in the lowermost stratosphere.

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[4] *Murphy et al.* [1990] were the first to note ice saturation above the tropopause, in this case in high latitudes in winter, and they proposed that ozone in this region was susceptible to heterogeneous chemistry that could enhance reactive chlorine. Subsequent studies have revealed a relatively small number of supersaturation events above the tropopause at lower latitudes [*Gierens et al.*, 1999; *Goldfarb et al.*, 2001; *Keckhut et al.*, 2005]. *Avallone et al.* [1993a], on the basis of a balloon profile obtained over New Mexico (34°N, 104°W) on 31 March 1991, found CIO abundances immediately above the tropopause to be considerably larger than could be explained by a model that included NO_x-reducing reactions on background aerosols [*Brasseur et al.*, 1990; *Rodriguez et al.*, 1991]. Subsequent ER-2 observations in aerosol influenced by emissions from Mount Pinatubo revealed CIO enhancements over a broad region of the lowermost stratosphere [*Avallone et al.*, 1993b] as well as in a very narrow cold layer slightly above the thermal tropopause [*Keim et al.*, 1996]. *Borrmann et al.* [1997] detected apparent CIO enhancements in a layer with enhanced particulates (volcanic and cirrus) near the midlatitude tropopause. More recently, *Smith et al.* [2001] analyzed a large number of transits of the ER-2 through the midlatitude tropopause and found that supersaturation and hence particles were very rare above the thermal tropopause. On the basis of average CIO abundances that were rarely above the detection limit of a few ppt, they concluded that chlorine activation near the tropopause at midlatitudes was unlikely, perhaps because of the rarity of water supersaturation above the thermal tropopause.

[5] In the lowermost stratosphere, total available inorganic chlorine, Cl_y, varies greatly with altitude as chlorine atoms are released from organic forms by exposure to ultraviolet radiation. Consequently, even though the partitioning between the various forms of inorganic chlorine may remain relatively constant over wide ranges of latitude and altitude [e.g., see *King et al.*, 1991; *Avallone et al.*, 1993b], variations in CIO are observed solely as the result of changes in Cl_y, especially when there is vertical transport of air. The situation is quite different at higher altitudes in the winter polar vortex, where organic forms of chlorine are largely absent and where inorganic chlorine, Cl_y, varies little with altitude. There, changes in CIO alone reflect changes in the partitioning between active (e.g., CIO_x) and reservoir (e.g., HCl and ClONO₂) forms of chlorine. To separate these confounding factors, *Thornton et al.* [2005] pioneered the use of the [CIO]/[Cl_y] ratio, a quantity that is predicted to not vary substantially at any particular altitude and latitude (e.g., photochemical environment) in the absence of heterogeneous chemistry, to identify chlorine activation in a data set from the Arctic near-tropopause region. They found the largest enhancements in [CIO]/[Cl_y] where temperatures were below ~208 K, ozone below 200 ppb, and where surface areas were well above the background aerosol average of ~1.0 μm² cm⁻³ in volcanically quiescent years [*Hoffman and Solomon*, 1992; *Deshler et al.*, 2003].

[6] Recent observations of HCl from the NASA WB-57F by *Marcy et al.* [2004] found much lower abundances of this inorganic chlorine reservoir in the low-latitude tropopause region, than were inferred from previous observations [*Farmer et al.*, 1976; *Lazrus et al.*, 1977; *Gandrud and Lazrus*, 1981]. Consequently, active forms of chlorine may

represent a more significant fraction of the total inorganic chlorine budget than previously believed at these latitudes and altitudes. Here, we examine measurements of CIO from a flight of the WB-57F near the midlatitude tropopause during the WB-57F Aerosol Mission (WAM) on 11 April 1998. Following an approach similar to that described by *Thornton et al.* [2005], we will estimate the [CIO]/[Cl_y] ratio, an indicator of chlorine activation by heterogeneous processes, and examine the factors that may have led to apparent significant activation in a region that was influenced by relatively large particulate surface areas.

2. Methods

2.1. Measurements

[7] The measurements presented here are from WAM, during which flights were conducted out of Ellington Field, Houston, Texas, in April and May of 1998. CIO was measured in situ using the CORE (Chlorine Oxides in Rocket Exhaust) instrument developed at the University of California, Irvine, and integrated in the instrument pallet area on the underside of the aircraft fuselage. CIO was measured by vacuum ultraviolet resonance fluorescence of chlorine atoms produced by rapid titration of CIO by nitric oxide, a technique used for several decades of measurements in the stratosphere [e.g., *Anderson et al.*, 1977; *Brune et al.*, 1988; *Toohey et al.*, 1993; *Pierson et al.*, 1999]. CORE was configured for fast response measurements (up to 25 Hz) of extremely high CIO abundances in the exhaust of solid fuel rockets for the coincident RISO (Rocket Impacts on Stratospheric Ozone) mission [*Ross et al.*, 2000]. Consequently, inside of plumes, continuous high-frequency measurements were obtained by continuous addition of nitric oxide (prepurified to 99.999% by passing through an Ascarite trap), whereas outside of plumes CIO abundances were measured using the well-documented approach of monitoring fluorescence signal from a flow of ambient air in the presence and absence of nitric oxide. The flow of nitric oxide was varied over a factor of ten to verify optimal conversion, and the measurements from three independent detection axes with separate excitation lamps were compared to ensure overall accuracy was within the quoted uncertainties.

[8] The detection method and geometries employed in CORE, and data analysis methods were identical to those of the balloon instrument launched from New Mexico on 31 March 1991, and the data analysis followed the procedures described there [*Toohey et al.*, 1993; *Avallone et al.*, 1993b]. One of the detection axes employed during WAM/RISO was specifically designed for optimal precision in rocket plumes. Therefore it used a relatively new source lamp that had nearly ten times the radiant flux of the others, thus providing the best signal-to-noise ratios in rapidly varying plumes, as well as under conditions of low ambient CIO. Although of lower precision, the measurements using the other two lamps were used to validate those of the higher-precision detection system. The results under background conditions, corroborated in the plumes of five rockets for which all three detection axes exhibit extremely high S/N ratios (better than 100:1), indicated that the independent laboratory calibrations of the three axes agreed to better than 10%.

[9] Although the CORE instrument shares detection and optical schemes with its aircraft and balloon predecessors, there is one significant difference, and that is a right-angle bend of the air stream prior to the detection system, as was necessary in order to integrate the instrument into the fuselage of the WB-57F. The novel two-stage inlet system was machined to specifications based on detailed computational fluid dynamical calculations of various configurations that were optimized to minimize contact of sampled air with instrument surfaces (D. Toohey, unpublished results, 1998). As was done with previous instruments designed to measure CIO [e.g., *Brune et al.*, 1988], surfaces that could be in contact with air to be sampled were coated with a substance (in this case, halocarbon wax) proven to be inert to Cl and CIO [Toohey et al., 1993]. Detailed laboratory tests found minimal losses (<2%) of Cl and CIO under flight conditions (temperatures, pressures, and flow rates). Consequently, we are confident that the CIO measurements obtained with this instrument, including those presented elsewhere [Ross et al., 2000; Popp et al., 2002], are accurate to within $\pm 20\%$ (1σ). Details of laboratory calibrations and data reduction techniques that were employed here are provided elsewhere [Brune et al., 1988; Toohey et al., 1993].

[10] The minimum time resolution for the CIO observations reported here was 20 s, representing a single measurement cycle consisting of 10 s of signal obtained in the presence of nitric oxide and 10 s of background. However, as before [Thornton et al., 2005] in this paper where we are mainly interested in variations of $[\text{CIO}]/[\text{Cl}_y]$ near the tropopause where CIO abundances are small, the measurements are time averaged in order to improve the precision to a magnitude smaller than the overall accuracy for all possible abundances. Thus, for a precision of about 1–2 ppt, we have averaged the data for 5 measurement cycles (100 s). This results in a horizontal resolution of approximately 20 km due to the nominal 180 m s^{-1} airspeed of the WB-57F. Other observations that are reported at shorter time intervals are time-averaged to coincide with the CIO observations.

[11] We use total water measurements from the NOAA Aeronomy Laboratory Lyman- α hygrometer [Kelly et al., 1989], an instrument that had a long legacy of measurements on the ER-2 aircraft prior to WAM and for which the results are accurate to 10% [Kley et al., 2000]. There were also observations from the JPL Laser Hygrometer (JLH), which are generally in good agreement with the NOAA instrument (although slightly higher by ~ 0.5 –1 ppm), but because this instrument had just been integrated on the WB-57F and has very recently undergone extensive calibrations that will result in slight downward adjustment of some data (R. Herman, personal communication, 2006), we have elected to use the more conservative NOAA results (i.e., slightly lower mixing ratios). The small differences are inconsequential for the discussion here, insofar as humidities were always below ice saturation regardless of the choice of measurement.

[12] Ozone was measured in situ by using a dual beam ultraviolet ozone photometer developed by the NOAA Aeronomy Lab [Proffitt and McLaughlin, 1983; Proffitt et al., 1989]. Data are reported every second, with an overall uncertainty of 5%. Particulate measurements were

provided by the University of Denver instrumentation [Wilson et al., 1991]. The Nucleation Mode Aerosol Size Spectrometer (NMASS) provided condensation nuclei counts, and particle size distributions [Brock et al., 1995]. The Focused Cavity Aerosol Spectrometer (FCAS) III provided surface areas and volume concentrations, which were used along with water measurements to calculate sulfate content (assuming particles are H_2SO_4 and water) [Jonsson et al., 1995].

[13] Temperature and pressure were measured on the WB-57F using the PT system, accuracy at 1 Hz is approximately 0.5 degree and 0.5 mbar. Tropopause height and potential temperature isentropes were determined by the Microwave Temperature Profiler (MTP) instrument operated by the NASA Jet Propulsion Laboratory [Denning et al., 1989]. The time resolution of the MTP instrument is 15 s.

2.2. Estimating Cl_y

[14] There is really only one way to absolutely know Cl_y in the midlatitude stratosphere, and that is by measuring and summing all of its components, or at least those that make up the vast majority of Cl_y (thought to be HCl, ClNO_3 , CIO and HOCl). To date there are no in situ measurements of HOCl in the lowermost stratosphere and at the time of the WAM campaign, only HCl had been measured in this region of the atmosphere with marginally adequate precision to detect abundances there (less than 100 ppt [Webster et al., 1993]). Unfortunately, in 1998 the WB-57F had yet to be outfitted with such an instrument, and there were no measurements of any inorganic chlorine species other than CIO.

[15] The stratospheric chemistry community has commonly used a surrogate for Cl_y that relies on measurements of a critical suite of organic compounds, including CF_3Cl , CF_2Cl_2 , and a variety of less abundant species. Observations of these species in the stratosphere are differenced from their values in the upper troposphere, and the sum of all is then referenced to a suitable long-lived tracer such as N_2O [Woodbridge et al., 1995]. Species that are known to contribute to Cl_y , but are difficult to measure, are inferred using correlations with other species that are routinely measured. Repeated observations of these correlations have shown relatively uniform relationships at particular latitudes, such that it is now a widely used method for inferring Cl_y in the lowermost stratosphere [e.g., Woodbridge et al., 1995; Engel et al., 2002]. Detailed modeling studies [Avallone and Prather, 1997] support the notion that near-linear correlations between two relatively long-lived species such as Cl_y and O_3 is a reasonable expectation in this region of the atmosphere.

[16] Unfortunately, at the time of WAM no instruments to measure N_2O or organic chlorine species had yet been developed for the WB-57F. However, over the next few years instruments to measure organic chlorine and HCl were developed and flown on the WB-57F. Thus we employ correlations of these species with ozone, a species which is also relatively long lived in this region of the atmosphere and that was measured during WAM, to estimate values of Cl_y appropriate for conditions encountered during WAM. This approach was first used by Avallone et al. [1993a] after it was observed that CIO abundances in the lowermost stratosphere were strongly correlated with ozone, presum-

ably because of the strong correlation of Cl_y with O_3 coupled to a fairly uniform ratio $[\text{ClO}]/[\text{Cl}_y]$ in the absence of significant chlorine activation.

[17] Recognizing the limitations of different approaches to estimating Cl_y , we have chosen here to use two in order to bracket the most likely values.

[18] For a lower limit estimate of Cl_y , we use the relationship between HCl and O_3 presented by Marcy *et al.* [2004] from a WB-57F flight in July 2002 that covered nearly the same latitude range (24–39°N) as our 1998 flight. Recent simultaneous measurements of HCl and ClONO_2 in the subtropics show few instances where $\text{ClONO}_2 > 10\%$ HCl from 12 to 18 km [Marcy *et al.*, 2005]. Thus we assume that under relatively low particulate surface areas encountered in July 2002, HCl would have represented at least 90% of inorganic chlorine, such that by assuming $[\text{Cl}_y] \sim [\text{HCl}]$, we allow for Cl_y to be as low as the HCl measurements themselves. We refer to this value of inorganic chlorine as $\text{Cl}_y(1)$, which, from a linear regression of the Marcy *et al.* HCl and O_3 observations, can be written as:

$$\text{Cl}_y(1) \sim [\text{HCl}] = 5.1 \times 10^{-4}[\text{O}_3] - 0.025 \quad (1)$$

[19] We have not adjusted the HCl estimate for a possible increase with latitude; however, as shown by Marcy *et al.* [2004, Figure 1c], model results for 46°N are not substantially different for the region where ozone <200 ppb, values that were encountered on 11 April 1998. Nor have we tried to account for any trends in inorganic chlorine that occurred between 1998 and 2002, as this was a period where total inorganic chlorine abundances were relatively constant [WMO, 2003].

[20] A second estimate of Cl_y , one that is considerably larger than $\text{Cl}_y(1)$, is based on several September 1999 measurements of halocarbons by the Lightweight Airborne Chromatograph Experiment (LACE) gas chromatograph, the earliest WB-57F flights where halocarbons were measured. LACE is a three-channel gas chromatograph that measured in situ CFC-11, CFC-12, CFC-113, CH_3CCl_3 , and CCl_4 every 70 s with an accuracy of 1–2% and a precision of 0.5–1%. Tracer correlations account for contributions from CH_3Cl and HCFC-22 ; the sum of these species and those measured is called organic chlorine, or CCl_y . Cl_y is determined by subtraction of this CCl_y from total chlorine which is calculated from tropospheric trends of chlorine source gases [Montzka *et al.*, 1996] and a mean age of air spectrum [Hall and Plumb, 1994]. In the auxiliary material,¹ we show the observed relationship of ozone and Cl_y as provided by LACE. From this, we derive the following empirical relationship for our second estimate of Cl_y :

$$\text{Cl}_y(2) \sim 6.7 \times 10^{-4}[\text{O}_3] \quad (2)$$

[21] One issue in this second approach is that below a potential temperature of ~ 380 K, isentropic mixing creates spread in any nonlinear tracer-tracer correlations [e.g., Avallone and Prather, 1997]. Because we have assumed a

linear fit to the data to extrapolate to lower potential temperatures we may have underestimated Cl_y below 380 K because of a possible underestimate for the transport of inorganic chlorine across the tropopause.

[22] These two estimates of Cl_y encompass a range of 150–250% from ozone values of 300 ppb to 100 ppb. This is far larger than the uncertainty in the ClO measurements and ultimately the uncertainty that limits our ability to accurately quantify the extent of chlorine activation. We note several important issues here that will be explored in detail later. First, enhanced ozone losses in air masses that experience continuous or repeated chlorine activation will result in an underestimate of Cl_y based on any correlation with ozone. Given the factor of 1.5–3 encompassed by $\text{Cl}_y(1)$ and $\text{Cl}_y(2)$, such ozone loss would have to be significant, of order 50–67%, but this cannot be ruled out (although such ozone losses at midlatitudes would be extremely noteworthy). Second, and perhaps more pertinent to this analysis, our analysis ignores recent injections of inorganic chlorine from the tropopause. There is no straightforward way to assess this process, other than to recognize that it also means that we necessarily have a lower limit for Cl_y , particularly in the case of the HCl/O_3 correlation.

3. Observations

[23] On 11 April 1998, the WB-57F departed Ellington Field (29°N, 95°W) at ~ 53000 UT (around 11 am Central Daylight Time), flew north-northwest along a great circle route at 17–18 km, reaching 46°N, 108°W at 65000 UT, then returned to Ellington Field. During the return portion of the flight, two profiles (descents) into the tropopause region (~ 12 km) were made. These descents occurred between 66000 and 70500 UT, or between 1 and 2 pm Mountain Daylight Time (Figure 1b). The minimum altitude of the first was reached at 42°N, 105°W, over southeastern Wyoming, after severe turbulence forced the WB-57F to descend to restart one of the engines. The minimum of the second was reached at 39°N, 102°W over western Kansas. Following the second dive, the remainder of the return portion of the flight was at 16 km.

[24] Observations of ClO , total water, particulate surface areas, $[\text{ClO}]/[\text{Cl}_y(1)]$, $[\text{ClO}]/[\text{Cl}_y(2)]$ and ozone for the entire flight are shown in Figures 1a and 1b. Three segments of the flight, high-altitude outbound, vertical profiles, and medium altitude return, are clearly distinguishable in the $[\text{ClO}]/[\text{Cl}_y]$ ratios. The highest reactive chlorine enhancements relative to available Cl_y (e.g., activations of 20% and larger) are observed closest to the tropopause (defined by lowest ozone values and largest total water) during the profiles, with considerably smaller, but still discernible, enhancements during the return at 16 km. The first half of the flight at 17–18 km generally exhibits very low $[\text{ClO}]/[\text{Cl}_y]$ ratios of 1–3% typical of regions where partitioning is determined by gas phase processes [King *et al.*, 1991]. During this portion of the flight (17–18 km) the aircraft also encountered a filament of air apparently of polar vortex origin, where ozone exceeds 1000 ppb, total water is <5 ppm, and particulate surface areas and number densities of condensation nuclei (CN) are relatively low ($\sim 1\text{--}3 \mu\text{m}^2 \text{cm}^{-3}$ and less than 100cm^{-3} , respectively). Although some of the largest absolute abundances of ClO

¹Auxiliary materials are available in the HTML. doi:10.1029/2006JD007640.

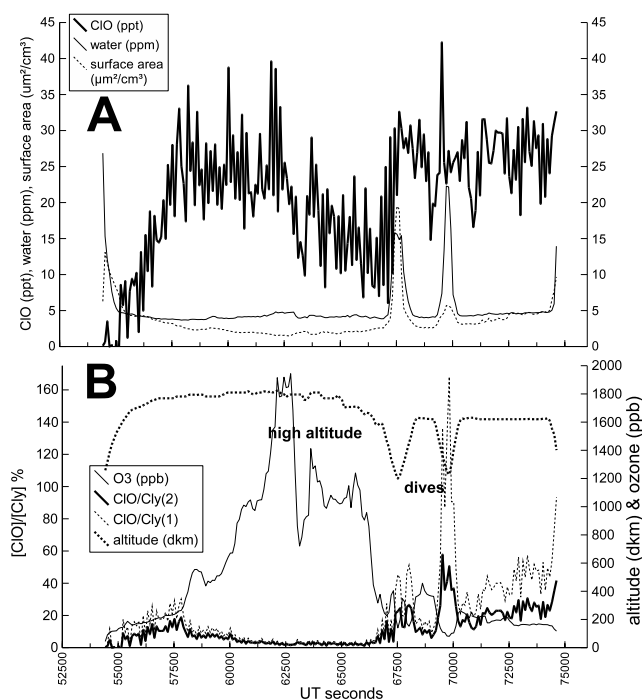


Figure 1. (a) CIO (ppt), water (ppm), and surface area ($\mu\text{m}^2 \text{cm}^{-3}$) for the 11 April 1998 flight. (b) $[\text{ClO}]/[\text{Cl}_2(1)]$, $[\text{ClO}]/[\text{Cl}_2(2)]$, and ozone for 11 April 1998 flight, and altitude of the aircraft (dkm; 1 km = 100 dkm). See text for description of $[\text{Cl}_2(1)]$ and $[\text{Cl}_2(2)]$. The three main flight segments, (1) 17–18 km outbound, (2) dives to thermal tropopause ~12 km, and (3) 16 km return, are marked.

observed on the flight, up to 30 ppt, occur in this region, in relation to the much larger amounts of Cl_y available (e.g., 1–2 ppb), the $[\text{ClO}]/[\text{Cl}_y]$ values in this filament are consistent with partitioning expected from gas phase chemistry alone. Similar CIO abundances later in the flight at lower altitudes are in a dramatically different region of the atmosphere, as can be seen in the water, particulate, and CN observations shown in Figures 1 and 2, thus dilution and downward mixing of the vortex filament does not appear to have occurred.

[25] It is worth considering here another explanation for the relatively high CIO abundances observed near the tropopause, namely the possibility that Cl_y could have been enhanced by the recent transport of very short lived (VSL) halocarbon species across the tropopause [e.g., WMO, 2003; Tuck *et al.*, 2004a; Ridley *et al.*, 2004]. Although the magnitude of this VSL flux is unknown, it seems highly improbable that it could deposit several ppb of Cl_y that would be required to maintain a constant $[\text{ClO}]/[\text{Cl}_y]$ ratio of a few percent throughout the flight. However, we might expect some additional Cl_y from VSL sources, and this may explain why we observe some air masses with $[\text{ClO}]/[\text{Cl}_y]$ greater than 100% (although precision of the CIO measurements and uncertainty in Cl_y are the more likely causes).

[26] Figure 2 magnifies the vertical profiles. In Figure 2a, we have plotted CIO and two calculations of $[\text{ClO}]/[\text{Cl}_y]$. CIO abundances in this region were 20–30 ppt, well above the averages of a few ppt previously reported near

the midlatitude tropopause [Smith *et al.*, 2001; Thornton *et al.*, 2003] and well above values expected from gas phase chemistry or chemistry on surfaces of particles in background aerosol. For both Cl_y estimates the $[\text{ClO}]/[\text{Cl}_y]$ ratios increase strongly approaching the tropopause, even briefly exceeding 100% for the lower of the two Cl_y estimates. CIO clearly does not exceed Cl_y , so given the significantly larger uncertainty in Cl_y , the discrepancy is most likely an indication that the HCl-O_3 relationship assumed for $\text{Cl}_y(1)$ underestimates the true inorganic chlorine. Nevertheless, if we have adequately bracketed the Cl_y with our two estimates, nearly 50% or more of the available inorganic chlorine has been activated at the tropopause at this location (69500–70000 UT). Such values rival those observed in midwinter at higher altitudes in the polar vortices and are consistent with predicted percent activations from model studies [Solomon *et al.*, 1997].

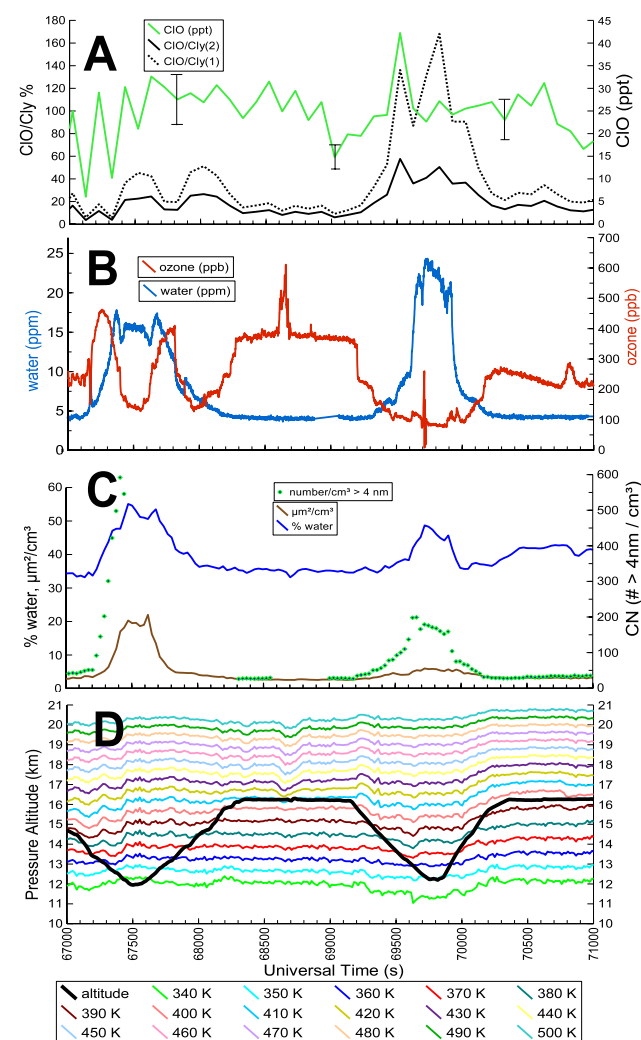


Figure 2. Magnified flight segment showing tropopause dives. (a) CIO and $[\text{ClO}]/[\text{Cl}_2(1)]$, $[\text{ClO}]/[\text{Cl}_2(2)]$. Each CIO data point covers ~500 m of altitude during the dives. Typical error bars are shown for CIO (1σ). (b) Water (ppm) and ozone (ppb). (c) Particulate surface area ($\mu\text{m}^2 \text{cm}^{-3}$), condensation nuclei count (cm^{-3}), and particulate % water content by mass. (d) Pressure altitude (km) and potential temperature (K) isentropes from 340–500 K.

[27] Figure 2b shows water and ozone which are somewhat anticorrelated in the tropopause dives; however, given that the thermal tropopause was at ~ 12.5 km, it is clear that substantial water was present throughout the first kilometer above the tropopause. Even so, relative humidities (with respect to ice) only reached $\sim 50\%$, indicating that cirrus clouds were not present at the time of the measurements. Figure 2c shows particulate surface area, mass-percent water, and CN. Surface area and mass-percent water are strongly correlated in the dives, and CN increased far beyond typical stratospheric values of ~ 30 cm $^{-1}$ as the WB-57F approached the tropopause, suggesting recent mixing of tropospheric air. Consistent with this notion, particulate surface areas reached $15\text{--}20$ μm^2 cm $^{-3}$, with number densities exceeding 500 cm $^{-3}$.

[28] Finally, Figure 2d shows altitude, potential temperature (Θ), and isentropes from 340 to 500 K along the flight path. Potential temperature in the first dive was as low as 330 K.

[29] In the dives, and to a lesser extent at 16 km on the return segment, a large increase in fine particles in the $0.1\text{--}0.15$ μm size range was noted. Vertical mixing is strongly suggested from the strong tilt in the potential temperature isentropes near the dive regions (recall, this is also the region that displayed severe turbulence).

[30] By design, after the second dive, the WB-57F skirted the thermal and chemical tropopause during the return to Ellington Field. This flight segment shows considerably more activation of chlorine than on the outbound segment a few kilometers higher. Particulate surface areas on the inbound segment were also higher ($\sim 3\text{--}4$ μm^2 cm $^{-3}$) than those observed ($\sim 1\text{--}2$ μm^2 cm $^{-3}$) on the outbound, higher altitude, segment.

[31] On descent prior to landing, the WB-57F again passed through a layer that seemed to contain substantial active chlorine. This layer extended from about 12–15 km, but the descent into Ellington Field was considerably faster than the two earlier tropopause dives so there are fewer observations. However, this suggests that the $[\text{ClO}]/[\text{Cl}_y]$ enhancements were extensive, essentially from Wyoming to the Gulf of Mexico.

[32] Although no substantial enhancements in the $[\text{ClO}]/[\text{Cl}_y]$ ratio were observed on climbout from Ellington Field in the morning, this may be due to the characteristics of the ClO instrument, where 10–15 min are required to clear a nitrogen purge gas out of the nitric-oxide manifold when the instrument is first powered up. Thus levels of nitric oxide may have been too small to convert ClO to chlorine atoms for the first few minutes of flight. Therefore we cannot determine whether the activation observed later in the flight has occurred over many days or is the result of a very recent event.

[33] We examined other midlatitude and subtropical WB-57F flights for similar enhancements to the $[\text{ClO}]/[\text{Cl}_y]$ ratio as were observed on 11 April 1998, but found none with such dramatic enhancements. One tropical survey flight (4 May 1998) shows up to 10% activation sporadically in regions of small water and particulate enhancements (both in the range of 5–10 ppm and μm^2 cm $^{-3}$) along a flight path closely following the tropical tropopause (within a few hundred meters). Additionally,

we show one typical midlatitude flight in the auxiliary materials.

4. Discussion

[34] The conditions encountered by the WB-57F near the Rocky Mountains on 11 April 1998 were not typical of those encountered by other aircraft profiling near the tropopause. At higher altitudes, ozone, total water, and CN observations were all consistent with air of purely stratospheric origin. However, as the WB-57F descended at 67000–67500 UT, the anticorrelation of H_2O and O_3 that is normally seen in the lower stratosphere broke down just above the tropopause, with air at ~ 13 km (350–370 K) exhibiting characteristics of both the stratosphere ($\text{O}_3 \sim 300\text{--}400$ ppb) and the troposphere ($\text{H}_2\text{O} \sim 10\text{--}17$ ppm). At 12 km the aircraft encountered tropospheric air with low ozone (<100 ppb), high water vapor (16 ppm) and high CN (>150 cm $^{-3}$). This pattern is mirrored when the aircraft ascends back to 16 km.

[35] It is interesting that ClO does not vary widely during the flight. Upon entry into the lower stratosphere (based on ozone >100 ppb), ClO abundances increase to $\sim 10\text{--}20$ ppt, where they remain for most of the outbound leg. There is some positive correlation with ozone, as is normal in this region [e.g., King *et al.*, 1991; Avallone *et al.*, 1993b]. On the return leg, ClO abundances range mainly between ~ 20 and 30 ppt. The fact that ClO does not reflect the variations in Cl_y is somewhat unusual; however, we note that increasing ClO abundances with decreasing O_3 have been observed in the tropopause region of the Arctic [Thornton *et al.*, 2005], and $[\text{ClO}]/[\text{Cl}_y]$ values inferred there were $\sim 5\text{--}20\%$, based on Cl_y derived in a similar manner as $\text{Cl}_y(2)$. Because ClO abundances are relatively uniform and our Cl_y formulations are proportional to O_3 , the ratio $[\text{ClO}]/[\text{Cl}_y]$ varies inversely with O_3 in a manner that looks artificial at the lowest ozone values where Cl_y abundances are most uncertain.

[36] It is somewhat doubtful that Cl activation varies as significantly as these results suggest, especially for the $\text{Cl}_y(1)$ formulation. Consequently, we surmise that $\text{Cl}_y(1)$ significantly underestimates the true Cl_y at low ozone, and that the $\text{Cl}_y(2)$ formulation is more realistic, at least for our observations on 11 April 1998. Alternatively, it is intriguing to speculate on whether some inorganic chlorine was injected into the lowermost stratosphere along with water and other species found predominantly in the troposphere.

[37] Using the more conservative formulation $\text{Cl}_y(2)$, there remain interesting differences in $[\text{ClO}]/[\text{Cl}_y]$ between the two dives. It is possible that ozone was not a good tracer for Cl_y . For the $[\text{ClO}]/[\text{Cl}_y]$ values to be similar near the bottoms of the two dives, Cl_y would need to differ by $\sim 25\text{--}40$ ppt (would need to be higher in the second dive) for a given ozone. Such a difference is within the uncertainty of estimates of inorganic chlorine entering the stratosphere. Alternatively, ozone would have to differ by ~ 50 ppb (would need to be lower in the first dive) for a given Cl_y . If the true relationship between ozone and Cl_y is nonlinear, some differences seems possible, given that there appears to be considerably more mixing in the first dive than in the second based on ozone and H_2O .

[38] Another possible explanation for differences between the dives is that there were differential ozone losses in the

two regions. At these altitudes, ClO abundances of ~ 20 ppt could destroy nearly 1 ppb day^{-1} of ozone by reactions with a few ppt each of BrO and HO₂ (values consistent with observations at these altitudes and latitudes). If similar ClO abundances were present for several months or more without significant mixing, 50 ppb of ozone could have been destroyed. Although this may seem unlikely, support for this possibility comes from a multifractal scaling exponent analysis [Tuck *et al.*, 2004b] of the measurements expected to be tracers; in this case, the only available suitable measurements are ozone and potential temperature. A “perfect” tracer has a multifractal scaling exponent, $H_1 = 5/9$, or 0.56. On the 11 April 1998 WAM flight, $H_{1(\text{ozone})}$ was 0.41, while on the 7 May 1998 flight, which also flew north from Houston but did not encounter enhanced ClO, $H_{1(\text{ozone})}$ was 0.52. This result is an indication that ozone abundances were influenced by sources and sinks on 11 April 1998, possibly locally and/or due to chemical readjustment (e.g., oxidation of VSL halocarbons followed by ozone loss; see below for more on VSL halocarbons) occurring following transport of the sampled air across the tropopause [Tuck *et al.*, 2004a]. Further discussion of the multifractal scaling exponents can be found in the auxiliary material.

[39] A layer of significantly activated chlorine was reported by Keim *et al.* [1996], an event they referred to as “Pinatubo influenced” because it occurred at a time when layers of volcanically enhanced aerosols were still present in the lower stratosphere. It is useful to compare and contrast those observations with ours made five years later and during a period of volcanic quiescence. Temperatures were nearly the same for both cases, and the maximum chlorine activation occurred in regions where water vapor, particulate surface areas, and CN were significantly elevated relative to surrounding air and typical stratospheric values. The main difference was that in the 1993 observations particle diameters were around 1 to 4 μm , whereas in 1998 diameters were only ~ 0.1 to 0.15 μm . In both data sets, relatively high mixing ratios of water vapor and CN (over five times typical stratospheric background CN) strongly suggest significant tropospheric influence. Therefore it is reasonable to expect that the extents of activation may also be similar.

[40] Keim *et al.* [1996] report a [ClO]/[Cl_y] ratio of only 25%, whereas we infer values between 25% and 50% (using Cl_y(2), the more conservative of the two estimates). Keim *et al.* [1996] based their Cl_y on the relationship developed by Woodbridge *et al.* [1995]. At low Cl_y, however, the Woodbridge *et al.* [1995] formulation has a large systematic error of ~ 200 ppt due to uncertainties in the cross calibration of instruments, the destruction of HCFCs in the troposphere, and uncertainties in measurements of CCl_y. Such uncertainties were of relatively minor concern for chlorine activation in the polar vortex, where CCl_y is $< 20\%$ of Cl_y, but, as described in Woodbridge *et al.* [1995], they are highly problematic for studies near the tropopause. Keim *et al.* [1996] wisely adjusted their Cl_y by forcing it to zero for tropospheric values of the passive tracer N₂O. Nevertheless, if we use our formulations for Cl_y at ozone abundances observed by Keim *et al.* [1996] (290 ppb) in the enhanced ClO layer, we derive values that are one third and one half as large (123 ppt and 193 ppt for

Cl_y(1) and Cl_y(2), respectively) as the value derived by Keim *et al.* [1996]. Thus a more realistic range for the chlorine activation in the layer observed by Keim *et al.* [1996] is $> 45\%$ (for maximum ClO of 90 ppt), a result that is remarkably consistent with the 11 April 1998 observations.

[41] Such similarities beg the question of whether or not these activation events also share a common mechanism. For significant activation, heterogeneous reactions must convert HCl into active chlorine at a rate that exceeds the formation rate of HCl, which occurs primarily by the reaction of chlorine atoms with methane. The partitioning of chlorine atoms is determined by the reaction ClO + NO; consequently, abundances of NO_x are what determine the threshold rates at which heterogeneous chlorine reactions must occur in order for there to be chlorine activation. At these latitudes and seasons, NO_x is produced by photochemistry of HNO₃ at a rate of approximately tens of ppt per day. This rate is relatively fixed, as it is governed by OH abundances and photolysis that are determined by other processes. The rates of heterogeneous reactions, on the other hand, are strongly dependent on particulate surface areas and particle composition (e.g., surface reaction coefficients, or “gammas”) which are highly variable (e.g., see Figure 1).

[42] Isentropic back trajectories (shown in auxiliary material) from the online Goddard isentropic trajectory model [Schoeberl and Sparling, 1995], and based on NCEP/NCAR reanalyses [McPherson *et al.*, 1979; Randel, 1987; Nagatani *et al.*, 1988], indicate that air sampled on the return leg on 11 April 1998 had cooled significantly in the previous 12 hours (from about 226–228 K to 213–215 K). Thus it is reasonable to assume that the particles were becoming more water rich as temperatures dropped and surface areas were increasing in the \sim day leading up to the observations. Under these conditions, the probabilities of heterogeneous reactions involving HCl, ClONO₂, and HOCl would be increasing, and we might expect to see [ClO]/[Cl_y] respond in some way to variations in particles. In the WB-57F measurements reported here and in the Keim *et al.* [1996] measurements, back trajectories suggest that water was not supersaturated in the previous week, yet both saw significant chlorine activation. In both the Keim *et al.* [1996] study and the present study, the key parameter for chlorine activation in the lowermost stratosphere does not appear to be water supersaturation, but rather adequate particulate surface area and adequate water to deliquesce what particles are present to shift the aerosol average composition toward a higher water content.

[43] Chlorine activation above the few percent expected from gas phase or background aerosols begins, in the WB-57F measurements, at slightly warmer temperatures (~ 215 K) than were observed in the Arctic (~ 208 K) [Thornton *et al.*, 2005]. However, both the Arctic and midlatitude data show a drop to “gas phase and background only” levels of a few percent for [ClO]/[Cl_y] above ~ 220 K and ~ 215 K respectively. For the 11 April 1998 flight, [ClO]/[Cl_y(2)] averaged 25% for $197 \text{ K} < T < 215 \text{ K}$. Above 215 K, [ClO]/[Cl_y(2)] was essentially zero.

[44] In Figure 3 we plot [ClO]/[Cl_y(2)] versus aerosol surface area for the entire set of observations on 11 April 1998, as well as those reported by Keim *et al.* [1996] using our formulation for Cl_y(2). There appears to be a threshold

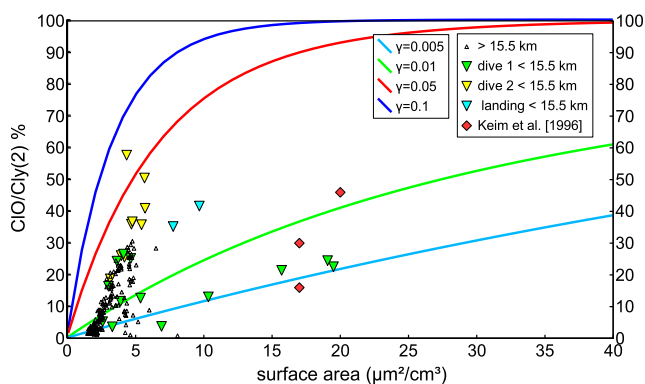


Figure 3. Particulate surface area and $[\text{ClO}]/[\text{Cl}_y(2)]$ for 11 April 1998 flight. (A plot of $[\text{ClO}]/[\text{Cl}_y(1)]$ is similar.) Additionally, the lower altitude portions of the flight (dives and landing) are highlighted. $[\text{ClO}]/[\text{Cl}_y(2)]$ data for the enhanced ClO layer observed by Keim *et al.* [1996] are also plotted for comparison. In the background, the amount of HCl activated in 3 sunlit hours on the given surface area for a range of potential γ values is shown.

value for particle surface areas at which $[\text{ClO}]/[\text{Cl}_y]$ increases sharply from a few percent, as is normally associated with gas phase partitioning, to 10–60% over a very narrow surface area range of 2–5 $\mu\text{m}^2\text{cm}^{-3}$.

[45] To examine the relationship between active chlorine and particle surface areas more closely, we have carried out photochemical (diel) model calculations (described by Thornton *et al.* [2005]) for conditions at 40°N and 16 km altitudes and initialized with measured ozone, temperature, H_2O , and calculated $\text{Cl}_y(2)$, with NO_y and CH_4 determined from correlations of these species with ozone [e.g., Avallone *et al.*, 1993a]. A steady state calculation that assumes a surface area of 0.5 $\mu\text{m}^2\text{cm}^{-3}$ is used to determine the initial partitioning of reactive species which are then used as input for a 1-day run at progressively higher particulate surface areas ranging from 1 to 20 $\mu\text{m}^2\text{cm}^{-3}$. These calculations were designed solely to assist in assessing the key parameters that could be responsible for activation of chlorine observed on 11 April 1998, and not as quantitative tests of any model parameters or to validate the measurements; therefore we will not go into more detail in this paper. However, they reveal some insights to the nature of chlorine activation and deactivation that are worth noting here and that may explain why previous investigators have failed to observe similar levels of activation at similar latitudes and altitudes.

[46] For prevailing conditions on 11 April 1998 at 16 km and below, model $[\text{ClO}]/[\text{Cl}_y]$ values remained below 2% for surface areas less than 1 $\mu\text{m}^2\text{cm}^{-3}$, but increased sharply from values of 2% to 30% for surface areas between 1.5 and 5 $\mu\text{m}^2\text{cm}^{-3}$. Activation reaches a maximum of ~60–70% for surface areas in excess of 10 $\mu\text{m}^2\text{cm}^{-3}$. This behavior is remarkably similar to that exhibited by the envelope of data points shown in Figure 3. The most significant reaction for chlorine activation in the model on the ~12 hour scale is $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$, the rate of which exceeded that of photochemical destruction of HNO_3 (by photolysis and reaction with OH) when surface areas exceed ~1.0 $\mu\text{m}^2\text{cm}^{-3}$ for the simulated heteroge-

neous reaction coefficient γ of ~0.05 (a value that is reasonable in light of the relatively large water content of the particles, e.g., Figure 2). Assuming a similar value for the reactivity coefficient of $\text{HCl} + \text{HOCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$, the rate of chlorine activation is enhanced by about 30–70%; however, this process does not directly influence partitioning in the NO_y family, the key to the maintenance of elevated ClO. Modeled ClO abundances are less than ~5 ppt so long as NO abundances remain above about 15–20 ppt, but once surface areas exceed 2 $\mu\text{m}^2\text{cm}^{-3}$ NO mixing ratios fall sharply from 15 ppt to less than 3 ppt at >5 $\mu\text{m}^2\text{cm}^{-3}$. This behavior is also consistent with the observations reported by Keim *et al.* [1996].

[47] Results of simple Langmuir calculations assuming reaction rate coefficients for HCl reacting with ClONO_2 and HOCl ranging from 0.005 to 0.1 (values based on liquid sulfate; values up to 0.3 have been reported [Kärcher and Solomon, 1999; Sander *et al.*, 2003; Meilinger *et al.*, 2005]), are shown in Figure 3 to illustrate that chlorine activation is apparently not limited by particulate surface areas. These calculations assumed a reaction time of only 3 hours, which is a very conservative lower limit, based on back trajectory analysis shown in the auxiliary material. It is more likely that activation has occurred for six hours or more, thus relaxing the values for heterogeneous rate coefficients or allowing for other rate limiting processes, such as availability of a limiting reactant that is photochemically produced. However, as noted from the detailed modeling described above, photochemical formation of oxidants such as ClONO_2 and HOCl do not seem to limit the conversion of HCl to active chlorine under these conditions, consistent with previous model studies [e.g., Solomon *et al.*, 1997].

[48] An interesting feature of the coupled ClO_x/NO_x chemistry in this region, as deduced from the photochemical model, is that rapid halogen activation is actually fueled by available NO_x . Upon an increase in particulate surface areas, as chlorine is activated by heterogeneous reactions it rapidly titrates NO_2 , which then produces additional ClO at a rate of two-to-one via $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$ (Cl_2 rapidly photolyzes in sunlight). Because NO is in rapid photochemical balance with NO_2 , if surface areas are sufficient, essentially all NO and NO_2 can be converted into HNO_3 within a few hours, while HCl is converted rapidly into active chlorine. Consequently, the variability in $[\text{ClO}]/[\text{Cl}_y]$ apparent in Figure 3 likely reflects a combination of factors, including variations in NO_y , available chlorine, heterogeneous reaction rate coefficients, times available for heterogeneous reactions to occur, poisoning at high surface areas [Hynes *et al.*, 2002], and/or particulate size limitations [Fluckiger *et al.*, 2000].

5. Conclusions

[49] We have reported on in situ observations of ClO from April 1998 that represent substantial chlorine activation in the lowermost stratosphere at midlatitudes. This represents the first clear evidence of inorganic chlorine enhancements outside of the polar regions under conditions unaffected by volcanic emissions. The chlorine enhancement appears similar to that which was reported previously and attributed to volcanic aerosols by Keim *et al.* [1996]. In

both cases, sampled air exhibited characteristics of both the stratosphere (e.g., relatively high ozone) and the troposphere (e.g., relatively high CN and water vapor), suggesting that high levels of water vapor may be necessary to produce adequate surface areas for activation, or to dilute particles sufficiently to enhance heterogeneous reaction rate coefficients of HCl with ClNO₃ and HOCl in order to compete with deactivation. Particulate surface areas in the range 5–10 $\mu\text{m}^2\text{cm}^{-3}$ and water content $\sim 40\%$ and larger appear to be sufficient to significantly activate chlorine.

[50] It is difficult to estimate the frequency of such chlorine activation events, but a hint is provided by the model calculations of Bregman *et al.* [2002], which show chlorine activation in a number of frontal regions and regions of uplift and mixing. On 11 April 1998, the breaking of gravity waves in the tropopause region may have been responsible for mixing of tropospheric and stratospheric air masses, a condition which may be necessary for producing sufficient surface areas and enhancing water content of particles such that heterogeneous activation of chlorine exceeds rates of deactivation by homogeneous processes. Nevertheless, these observations indicate that substantial activation does not require volcanic conditions nor the formation of large ice crystals (e.g., cirrus), and therefore may be more prevalent than previously assumed. The conditions required for midlatitude chlorine activation may simply be uplift and mixing of moist tropospheric air with lowermost stratospheric air near the extratropical tropopause; this is not an unusual or rare feature [Foot, 1984; Dessler *et al.*, 1995; Tuck *et al.*, 1997; Hegglin *et al.*, 2004; Krebsbach *et al.*, 2006]. Three-decade long balloon observations of stratospheric aerosol suggest that enhanced particulate layers are a common feature in the tropopause over southeastern Wyoming [Deshler *et al.*, 2003].

[51] If chlorine activation in the tropopause region is more common than is presently assumed, it may have some bearing on the trends that have been observed in this region [Logan *et al.*, 1999]. Thus it would be useful to carry out surveys of ClO and inorganic chlorine (e.g., HCl and ClNO₃) with instruments capable of measuring ppt abundances of these species. As the chlorofluorocarbons are replaced by chlorine-containing compounds that decompose in the lowermost stratosphere, an accurate assessment of the impacts of such compounds on future ozone trends will require adequate treatment of the partitioning of reactive chlorine in the tropopause region.

[52] **Acknowledgments.** Back trajectories were calculated using the Goddard Online Trajectory Model, for which we thank Mark Schoeberl, Leslie R. Lait, and Paul Newman of NASA Goddard. Stephen Donnelly assisted with ClO measurements during WAM. We thank Fred Eisele of NCAR, Marty Ross of the Aerospace Corp. and Scott Shafer of UC Irvine for assistance with inlet development and fabrication. We thank the WB-57F air and ground crews. Funding for D. Toohey to participate in WAM was provided by NSF grants ATM-9258040 and ATM-9732909. B Thornton was supported by NSF grant ATM-9978181. The WB-57F measurements during WAM and ACCENT were funded by the NASA UARP and AEAP, managed by Mike Kurylo and Donald Anderson, respectively. Work performed by M.J.M. at the Jet Propulsion Laboratory, California Institute of Technology, was done under contract with the National Aeronautics and Space Administration.

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